

IONOGENIC HYDROPHILIC WATER-INSOLUBLE GELS FROM PARTIALLY HYDROLYZED ACRYLONITRILE POLYMERS AND COPOLYMERS, AND A METHOD OF MANUFACTURING SAME

The new hydrogels are either non-crosslinked or crosslinked by crosslinks formed by side-reactions of nitrile groups with strong bases; This kind of crosslinking can be either supplemented or replaced by usual covalent crosslinking, or also by ionic crosslinking, using polyvalent cations as crosslinking agents.

The hydrogels of the invention are noted for their extraordinary strength, inertness in contact with having tissues, permeability for gases and solutes as well as for their electrochemical characteristics. They are therefore utilizable in surgery, in density and in various fields of chemical technology.

The preferred method of manufacturing the above defined kind of hydrogels consists in subjecting acrylonitrile-containing polymers or copolymers with at least 80% of acrylonitrile units to a homogeneous controlled partial alkaline hydrolysis in solutions of said polymers in aqueous or lower alcoholic solutions of lithium, sodium or calcium rhodanides, using strong inorganic or organic bases as alkaline catalysts or hydrolytic agents. The hydrolysis can be carried out at any temperature between the melting and boiling point of the solution, usually between about -15° and $+130^{\circ}$ C, preferably between about 0° and $+25^{\circ}$ C.

BACKGROUND OF THE INVENTION

The alkaline hydrolysis of polyacrylonitrile is well known, it was, however, usually carried out in heterogeneous systems using as starting material undissolved, either non-swelled or only slightly swelled polyacrylonitrile in bulk—e.g. sheets—or in the form of a powder. The alkaline hydrolysis of polyacrylonitrile takes place at a comparatively high rate so that solid polymer is hydrolyzed gradually, layer by layer. If the alkaline hydrolysis or saponification was performed thoroughly, the product consisted almost entirely of the corresponding salt of polyacrylic acid. More often, however, the product was a varied mixture of copolymers of acrylic acid with acrylonitrile, containing moreover various cyclic and crosslinked components, particularly if the starting polymer was high-molecular. Chemical composition ranged from almost intact polyacrylonitrile to almost pure polyacrylic acid, depending also on the molecular weight, the size of the particles of the starting polymer etc. Such heterogeneous hydrolysis never resulted in homogeneous gels of the above defined structure. As the hydrolyzates contained usually units of acrylic acid in a predominating amount, it was often supposed that the alkaline hydrolysis is a pure saponification where nitrile groups are immediately transformed to carboxylic ones, the step characteristic for acid hydrolysis leading to amide group being avoided. In the practice, only low-molecular polyacrylonitrile was used for the alkaline hydrolysis, yielding water-soluble products which are utilized as textile sizes, antistatic preparations in the manufacture of synthetic fibres etc.

On the other hand it is known that homogeneous acid hydrolysis of polyacrylonitrile or its copolymers with at least 80% of acrylonitrile units can be controlled in such a way that a multi-block copolymer with high strength

and elasticity is formed as a result of the prevailing "zipper-like" step of the hydrolysis. Said multi-block copolymers contained, in addition to intact polyacrylonitrile sequences, comparatively long sequences consisting almost entirely of acrylamide units. Only at high conversions, and particularly at high temperatures of the hydrolysis, the hydrophilic segments contain also some units of acrylic acid and diacryl imide. It has been suggested to increase the portion of acid units therein by additional alkaline hydrolysis or by a treatment with nitrous acid, but most of the amide groups remained intact due to steric hindrances and the end products were different both qualitatively and quantitatively from the hydrogels of the present invention.

GENERAL DISCLOSURE

Alkaline hydrolysis of predominantly acrylonitrile containing polymers in homogeneous phase where the solvent or swelling agent is an aqueous or alcoholic solution of lithium, sodium or calcium rhodanides or of mixtures thereof, containing, if desired, minor amounts of other salts causing no coagulation, leads to ionogenic multi-block hydrophilic copolymers of a new class. In comparison with the known multi-block copolymers obtained by homogeneous acid hydrolysis of predominantly acrylonitrile containing polymers the new hydrogels contain in their hydrolyzed segments a major portion of acrylic acid units and a minor, but not negligible portion of acrylamide units. As a result, the new hydrogels are, in neutralized condition, more swellable at the same conversion of hydrolysis, or stronger than the known acid-hydrolyzed copolymers with the same content of water at swelling equilibrium, containing, in average, longer sequences of acrylonitrile units and thus larger polyacrylonitrile domains which are responsible for the strength of the hydrogel.

Further advantage of the present ionogenic hydrogels is the absence of diacryl imide groups which are suspected to hold some cations rather firmly so that the latter cannot be easily removed by washing. The behavior of weak cation exchanger, due to the presence of many carboxylic side groups, as well as the slightly ampholytic characteristics caused by weakly basic groups formed by side-reactions of nitrile groups, confer to the new hydrogels interesting electro-chemical properties.

The formation of the multi-block structure by the alkaline hydrolysis is surprising and cannot be derived from the known acid hydrolysis which possesses an entirely different reaction mechanism.

Thus, the object of the invention is a new class of ionogenic water-insoluble hydrogels, characterized by a multi-block structure with two distinct but inseparable phases, one of them being amorphous and strongly hydrophilic, consisting mainly of a major portion of acrylic acid units and of a minor portion of acrylamide units, the other phase consisting substantially of crystalline or quasi-crystalline polyacrylonitrile detectable by usual X-ray analysis, and further characterized by a minor amount of weakly basic nitrogenous groups and from 0 to about 5% (mol.) of crosslinks derived from transformed nitrile groups, said crosslinks being unstable in presence of free bases but stable, at mild temperatures, in neutral and acid media, and further containing, if desired, covalent crosslinks formed subsequently, or ionic crosslinks, each polymer chain containing, in average, more than one block or sequence of polyacrylonitrile and more than one block or sequence of the said